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Upgrading of bio-oil from biomass fast pyrolysis in China: A review

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ABSTRACT

Bio-oil is a brown liquid product from biomass fast pyrolysis. The upgrading of bio-oil has been a hotspot due to its contribution to the application of bio-oil. The properties of bio-oil, research progress, advantages and disadvantages of upgrading techniques of bio-oil from biomass fast pyrolysis in China are summarized, with the hope of promoting the development of upgrading and application of bio-oil in China. The upgrading techniques include hydrogenation, hydrodeoxygenation, catalytic pyrolysis, catalytic cracking, steam reforming, molecular distillation, supercritical fluids, esterification and emulsification. Also, the current problems are summarized and several future development directions of bio-oil upgrading are pointed out.

Contents

1. Introduction

With the diminishing supply of fossil fuels and increasing environmental concerns, biomass is considered to be a promising resource of global fuel production. Compared with fossil fuels, biomass energy, for example bio-oil, has great potential to be an alternative source of energy due to its advantages on reproducibility, resources universality [1] and environmental protection. Currently, producing biofuels, such as bio-oil, fuel gas and bio-char, through biomass fast pyrolysis has been a hotspot both at home and abroad. However, as a promising alternate energy source, direct application of bio-oil is limited due to its high viscosity, high water and ash

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Table 1
Comparison of selected properties of bio-oils derived from pyrolysis of rice husk and bio-oils derived from pyrolysis of wood and heavy petroleum fuel oil.

Properties		Bio-oils derived from pyrolysis of rice husk [9]	Bio-oils derived from pyrolysis of wood [10]	Heavy petroleum fuel oil [11]
Water content (wt%)		25.2	15–30	0.1
pH		2.8	2.5	–
Elemental composition (wt%)	C	41.7	54–58	85
	H	7.7	5.5–7.0	11
	O	50.3	35–40	1.0
	N	0.3	0–0.2	0.3
Ash		–	0–0.2	0.1
HHV (MJ/kg)		17.42	16–19	40
Viscosity (at 50 °C) (mPa s)		128	40–100	180
Solids (wt%)		–	0.2–1	1
Distillation residue (wt%)		–	Upto 50	1

contents, low heating value, instability and high corrosiveness [2], which leads to a series of problems in application of bio-oil.

So, in order to improve physicochemical properties of bio-oil for its practical application, upgrading of bio-oil is necessary. However, the process of upgrading of bio-oil is very difficult because of the complexity of the bio-oil contents [3]. Although biomass fast pyrolysis for bio-oil production has aroused extensive attention and interests both at home and abroad in recent years [4], there are also lots of unknown mechanisms to be clarified before bio-oil can be used easily [3].

This paper reviews the properties and present situation of upgrading technologies of bio-oil from biomass fast pyrolysis in China. The current problems of bio-oil upgrading in China are also summarized. Besides, some recommendations on the development directions are put forward based on the current status of upgrading of bio-oil, with the hope of promoting the improvement of upgrading and application of bio-oil in China.

2. Properties of bio-oil

Usually, bio-oil is a dark brown, free-flowing liquid with a distinctive smoky smell. Many publications [5–8] have reported the physical properties of bio-oils. Compared with petroleum-derived oils, the different chemical composition of oils results in different physical properties of bio-oils. Bio-oil is a complex mixture, which consists of several hundreds of organic compounds, mainly including alcohols, acids, aldehydes, esters, ketones, phenols as well as lignin-derived oligomers [2]. Thorough understanding of bio-oil is a necessary precondition for researchers to clarify mechanisms of properties and upgrading of bio-oil. Table 1 shows comparison of selected properties of bio-oils derived from pyrolysis of rice husk and bio-oils derived from pyrolysis of wood and heavy petroleum fuel oil.

As shown in Table 1, the water content of bio-oil derived from pyrolysis of rice husk is 25.2 wt%, while the values of bio-oils derived from pyrolysis of wood and heavy petroleum fuel oil are 15–30 wt% and 0.1 wt%, respectively. The oxygen contents in bio-oils derived from pyrolysis of rice husk and wood are 50.3 wt% and 35–40 wt%, respectively, while that in heavy petroleum fuel oil is 1.0 wt%. So, a conclusion can be drawn that pyrolysis bio-oils have much higher oxygen and water contents than heavy petroleum fuel oil, which leads to lower heating values in bio-oils than in heavy petroleum fuel oil. The corresponding HHV (MJ/kg) of bio-oils from pyrolysis of rice husk and wood is 16–19 MJ/kg, which is about 50% of that of heavy fuel oil (40 MJ/kg). The properties of heavy petroleum fuel oil are significantly different from bio-oils derived from the biomass pyrolysis processes.

According to Qiang et al. [12], it is known that the poor properties of bio-oil usually include high contents of water, oxygen, ash and solids, low pH values, high viscosity, chemical and thermal instability, low heating value, and poor ignition and combustion properties. For example, high oxygen content leads to thermal instability, which hinders the storage stability of bio-oil, and high acidity can result in corrosion of experimental facilities. Meanwhile, aldehyde and phenol in bio-oil are unstable, unsaturated, and easily form macromolecules through polymerization, especially in the acidic condition, which will also increase the viscosity of bio-oil and reduce liquidity. The application of bio-oil is so far limited by these undesired properties. During the production process of bio-oil, different biomass and reaction conditions can lead to bio-oils with different yield and quality. Despite these shortcomings of fuel properties, bio-oils also have some promising properties, such as less toxicity, good lubricity and greater biodegradation than petroleum fuels. Upgrading of bio-oil is therefore necessary to improve its properties for its practical application as liquid fuel.

3. Upgrading of bio-oil

Although fast pyrolysis can produce considerable amount of bio-oils, for example a yield up to 56.8% was reported in domestic research [13], their direct applications as fuels are limited by the problems of high viscosity, high oxygen content and corrosion, as well as their thermal instability. Therefore, bio-oils should be upgraded using proper methods before they can be used in diesel or gasoline engines.

3.1. Hydrogenation

The ultimate aim of hydrogenation is to improve stability and fuel quality by decreasing the contents of organic acids and aldehydes as well as other reactive compounds, because they not only lead to high corrosiveness and acidity, but also set up many obstacles to applications [14].

Recently in China, many researchers have achieved considerable progress in upgrading pyrolysis bio-oils using hydrogenation technology. Traditionally researchers generally upgraded bio-oil by single hydrogenation technology. Traditional hydrogenation is the treatment of pyrolysis bio-oil under specific conditions, such as high pressure (10–20 MPa), certain temperature and hydrogen flow rate as well as proper catalyst. The bio-oil can be obtained by various kinds of pyrolysis using several catalysts, such as Al_2O_3-based catalysts [15,16] and Ru/SBA-15 catalysts [17], etc. In the upgrading experiments, the following results [15,18] generally could be observed: the pH value, the water content as well as the H element content all increased in varying degrees while the dynamic viscosity decreased to some extent. These experiments also simultaneously indicated that the properties of the pyrolysis bio-oil were improved by hydrotreating and esterifying [16] carboxyl groups over these catalysts. At present in China, the largest scale of hydrogenation reactor is a cylindrical reactor with a depth of 120 mm and an inner diameter of 32 mm [16].

Recently a novel upgrading method named one-step hydrogenation–esterification (OHE) was established to convert acids and aldehydes to stable and combustible components [19]. The catalysts for OHE reaction were bifunctional, such as Al-SBA-15 supported palladium bifunctional catalysts [20] and bifunctional Pd catalysts [21], which means they have properties of hydrogenation and esterification [19,21]. This is the advantage over the

traditional hydrogenation process for OHE. Yu et al. [21] screened out 5% $Pd/Al_2(SiO_3)_3$ with the best catalytic performance among tested bifunctional catalysts, and demonstrated that it is viable to convert these unstable constituents of bio-oil to esters and alcohols through this simple and effective OHE reaction. Besides, for the OHE reaction, tests by Tang et al. [22] demonstrated the effectiveness of the bifunctional catalyst system for combined hydrogenation/esterification and a synergistic effect between metal sites and acid sites over respective catalysts. Moreover, some measures were taken to improve the catalytic performance of the bifunctional catalyst [23]. Obviously, the new hydrogenation method is much better than the traditional method due to the use of bifunctional catalysts.

3.2. Hydrodeoxygenation

Hydrodeoxygenation (HDO), a variant of catalytic pyrolysis, is a bio-oil upgrading process which removes the oxygen under high pressure of hydrogen with a catalyst. It can reduce oxygen content of many kinds of oxygenated chemical groups, such as acids, aldehydes, esters, ketones and phenols, etc. Hydrodeoxygenation has been considered to be one of the most promising methods for bio-oil upgrading [24]. Recently in China, a 500 ml autoclave reactor [24] with diameter of 10 mm and length of 420 mm is the largest experimental facility for hydrodeoxygenation. Additionally, the largest dosage of the catalyst for this kind of research is 1.5 g [24].

Most of the previous researches on hydrodeoxygenation of bio-oil focused on industrial NiMo or CoMo sulfide/supported hydrotreating catalysts. For instance, Wang et al. [24] demonstrated Pt supported on mesoporous ZSM-5 showed better performance than Pt/ZSM-5 and Pt/Al_2O_3 in dibenzofuran hydrodeoxygenation. However, these catalysts have several inherent shortcomings in hydrodeoxygenation, such as product contamination and catalyst deactivation. The noble metal catalyst exhibits high catalytic activity in the HDO reactions [24–26], but with high cost. So, novel and economical catalysts that can be used for hydrodeoxygenation of bio-oil with high oxygen content should be developed.

Due to excellent hydrodeoxygenation activity and selectivity in the catalytic reactions [27,28], amorphous catalysts have aroused a great attention in China recently. Wang et al. [27,28] prepared and tested hydrodeoxygenation activity of lots of amorphous catalysts, and demonstrated that Co–W–B had higher thermal stability than Ni–Co–W–B and Ni–W–B catalyst. And, the catalyst activity could be increased with the Co/Mo ratio increase of surface composition, which means the catalyst activity could be further improved at proper conditions. Therefore, this new kind of amorphous catalyst will be a potential candidate for the HDO process due to its many advantages, such as simple preparation, high thermal stability and high HDO activity as well as low cost [28,29].

3.3. Catalytic pyrolysis

Recently, catalytic pyrolysis has aroused a great interest for the advantages of operating at atmospheric pressure and the lack of need for hydrogen [30], which has been demonstrated by many researches. The experiments on catalytic pyrolysis of biomass were generally carried out in a fixed bed reactor [31] or fluidized bed [13] under nitrogen flow with some catalysts, such as HZSM-5 [13,31], ZSM-5 [32], Al-SBA-15 [32], alumina [32] and Cu [33], etc. So far in China, the largest scale of catalytic pyrolysis reactor is a tubular reactor with a length of 250 mm and an inner diameter of 38 mm. Many aspects of catalytic pyrolysis have been studied, including screening of feasible catalysts with high deoxygenating activities [32,34] or preferred selectivities [35], influence of temperature and catalyst-to-material ratio on product yields [13], characteristic analysis of obtained bio-oils using elemental, GC–MS and FTIR technologies [31]. Both in a fixed bed reactor [31,32] and in fluidized bed [13], the investigation indicated that catalytic pyrolysis lowered the oxygen content of the bio-oils and aggrandized the calorific values compared to the direct pyrolysis without catalysts. This conclusion can be drawn in many experiments with different biomass, including green microalga [31], corncob [13], herb residue [32] and waste woody biomass [33]. Besides, catalytic pyrolysis can lead to higher content of aromatic hydrocarbons in bio-oils with HZSM-5 [31], alumina [32] or HZSM-5/γ-Al_2O_3 [35] as catalyst while direct pyrolysis promoted the increase of carbon chain compounds [31]. However, Zhang et al. [13] reported that the addition of HZSM-5 zeolite catalyst in the experiments caused a significant decrease of heavy oil fraction and an increase of the coke, water and non-condensable gas yields. This was because the HZSM-5 zeolite catalyst could promote the conversion of oxygen element in heavy oil into CO, CO_2 and H_2O. So, choosing proper catalysts is crucial to catalytic pyrolysis.

Besides, some new reports on the catalytic pyrolysis were reported recently in China. During biomass pyrolysis, CaO addition could catalyze dehydration reactions [36]. $CaCl_2$ was reported to have an apparent catalytic effect on elephant grass pyrolysis [37] and polluting heavy metal Cu showed effective catalytic activity in the thermo-decomposition of biomass [33]. This research can contribute to the development of catalysts applied on the more efficient catalytic pyrolysis process.

Therefore, catalytic pyrolysis can promote the production and quality of bio-oils through using the appropriate catalysts. But, it also encounters some problems, such as catalyst deactivation, reactor clogging, coke production and high water content in bio-oils, etc.

3.4. Catalytic cracking

Recently in China, catalytic cracking for upgrading pyrolysis bio-oil can be divided into two patterns, the traditional catalytic cracking and the combination of catalytic pyrolysis and catalytic cracking. Traditionally, the catalytic cracking referred to a thermal conversion process of bio-oil under certain conditions, including hydrogen flow, proper catalysts (e.g., HZSM-5 [38]) and a specific temperature higher than 350 °C as well as rather high pressure. Hydrogenation with simultaneous cracking occurred during the catalytic cracking process. The products of the catalytic cracking process consist of solid, liquid and gases. The solid is called coke, and the liquid can be divided into two phases: aqueous phase and organic phase. The gas is combustible. In China, the traditional catalytic cracking had been carried out in a tubular fixed bed reactor [38] and micro-fixed bed reactor [39]. The advantage of this technique was the probability of obtaining a good deal of light product, but catalyst coke deposition was a bottleneck for sustainable application of catalysts (e.g., HZSM-5 [39]).

Compared to the traditional catalytic cracking, scholars in China made the combination of catalytic pyrolysis and catalytic cracking to upgrade pyrolysis bio-oil. It adopted a sequential biomass pyrolysis reactor which consisted of a traditional pyrolysis reactor followed by the subsequent apparatus that supported decomposition of gaseous intermediate [40]. The largest reactor for this kind of investigation was made of 316 stainless tube, with a length of 1000 mm and an inner diameter of 20 mm [38]. For example, Xiwei et al. [40] applied this method and found that biomass could be fully converted into gaseous products, such as H_2, CH_4 and CO, etc. Catalyst (Fe/γ-Al_2O_3) activities were affected by several factors, including calcination temperature, temperature of catalytic pyrolysis and Fe/Al mass ratio. Hong-yu et al. [41] demonstrated that when the cracking temperature was 500 °C, with a Weight Hourly Space Velocity of 3 h^{-1}, the liquid yield reached the maximum and the oxygenic compounds also

decreased obviously. To summarize, researches demonstrated that the combined process had the superiority of promoting the liquid yield and improving the fuel quality over the separate processes.

3.5. Steam reforming

Steam reforming was also an effective method to upgrade pyrolysis bio-oil. It could simultaneously produce renewable and clear gaseous hydrogen along with bio-oil upgrading, which was a big advantage for steam reforming among various upgrading technologies. Steam reforming generally used a fluidized bed reactor system [42] or a fixed bed reactor system [43]. The largest reactor system up till now in China is a two-stage fixed bed reactor system with the height of 800 mm and the inner diameter of 20 mm [42]. In the steam reforming process, high temperature (800–900 °C) and proper catalysts [44–48] were generally necessary.

However, coke formation caused catalyst deactivation, which was a big problem in steam reforming of the bio-oil for sustainable hydrogen production. Chen et al. [48] and Wu et al. [49] investigated carbon deposition behavior in the steam reforming process of bio-oil for hydrogen production and demonstrated that for the competition of carbon deposition and carbon elimination, a peak value of coking formation rate was obtained in a broad range of temperature (575–900 °C), while high ratio of steam to carbon contributed to the carbon elimination. Also, regenerated catalyst showed slight drops in activity due to Fe contamination and Ni redispersion [50]. Above all, upgrading bio-oil by steam reforming was feasible in China but more appropriate catalysts and dependable, steady and fully developed reactor systems still need to be developed in the future.

3.6. Molecular distillation

Bio-oil from biomass pyrolysis is a complex mixture of many chemical compounds with a wide range of boiling points. Due to the thermo-sensitive property of bio-oil, it is easy to undergo reactions such as polymerization, decomposition and oxygenation [51]. But, molecular distillation cannot be limited by these poor properties and be appropriate for the separation of bio-oil. So, molecular distillation is one of the most economically feasible methods to purify bio-oil.

Chinese researchers have carried out considerable work in upgrading bio-oil by molecular distillation. Wang et al. [51] separated bio-oil using KDL5 molecular distillation apparatus, demonstrated the feasibility of using molecular distillation to isolate bio-oil and came up with a separation factor to signify the ability of isolating the chemicals of bio-oil during the molecular distillation process. The complexity of bio-oil was confirmed by studying the chemical composition of the three fractions separated by molecular distillation using gas chromatography combined with mass spectrometry (GC–MS) [52]. The results showed that the light fraction consisted of CO_2, water, hydrocarbons and alcohols which evaporated fastest, while the heavy fraction had the highest char residue yield and the slowest rate of decomposition due to the existence of saccharides, phenols and the pyrolysis products, such as CO_2, alcohols and phenols. The middle fraction was similar to the heavy fraction except for the existence of water and formic acid. Using molecular distillation to refine biomass pyrolysis oil could upgrade the physical properties of the refined bio-oil [53,54], such as carboxylic acids content, water content and heating value.

In conclusion, molecular distillation is appropriate for the separation of bio-oil and is not restricted by its poor properties. However, due to the necessity of high vacuum condition, the energy consumption in the process is usually larger than conventional distillation, such as vacuum distillation, steam distillation, atmospheric distillation and flash distillation [51]. Besides, molecular distillation is currently suitable for the separation of heat-sensitive and high value-added substance, which limits the application of molecular distillation. To speak of, the molecular distillation apparatus is urgently needed on account of the fact that most of experimental facilities for relative investigation in China were directly imported from the foreign countries such as Germany.

3.7. Supercritical fluids (SCFs)

Recently, a new method for upgrading bio-oil from fast pyrolysis using supercritical fluids (SCFs) has drawn a great attention at home and abroad. This method takes full advantage of the unique and superior properties of supercritical reaction media, such as liquid-like density, faster rates of mass and heat transfer, dissolving power and gas-like diffusivity and viscosity [4]. SCFs can be not only used as a reaction condition to produce bio-oils, but also can be used as a superior medium to upgrade bio-oils, and have shown great potential for producing bio-oils with much lower viscosity and higher caloric values [2]. In order to enhance the oil yields and qualities, some organic solvents, such as ethanol [55–59], methanol [60–62], water [63] and CO_2 [64], etc., were adopted in many relative researches.

Usually, the upgrading method using SCFs performed effectively in improving the quality and yield with the help of some catalysts, such as aluminum silicate [65], HZSM-5 [66], bifunctional catalysts [67,68], etc. The upgrading experiments were mainly performed in the autoclave reactor, with a volume of 100 ml or 150 ml. After upgrading, the components of the bio-oil were optimized significantly and the properties of the bio-oil were improved greatly. The catalysts in supercritical media can facilitate the conversion of most acids into various kinds of esters in the upgrading process. As a result, kinematic viscosity and the density of upgraded bio-oil decreased compared to that of crude bio-oil, while the heating value and pH value of upgraded bio-oil increased to a certain degree [55,59,64]. Dang et al. [3] reported that higher initial hydrogen pressure (2.0 MPa) could effectively inhibit formation of coke. Although increasing temperature was helpful to promotion of heating value of upgraded bio-oil, the amount of desired products decreased and the formation of coke would be much more serious.

Although the process of upgrading bio-oil using SCFs is environmentally friendly, and can be carried out at a relatively lower temperature, it is not economically feasible on a large scale due to the high cost of the organic solvents [2]. Therefore, researchers in China should input more effort into testing less expensive organic solvents as a substitute for SCFs.

3.8. Esterification

Due to the drawbacks of pyrolysis bio-oil, such as low heating value, high viscosity, high corrosiveness and poor stability, upgrading of bio-oil before practical application is necessary to acquire high grade fuel. Organic acids in bio-oils can be converted into their corresponding esters by catalytic esterification and this greatly improves the quality of bio-oils [65].

Upgrading the bio-oil through catalytic esterification has been carried out widely in China. During the etherification process, the experiment was generally conducted in a 250 ml or 300 ml autoclave, and the catalysts included ion exchange resins [65], MoNi/γ-Al_2O_3 [69], etc. The results showed that the upgraded bio-oil had lower acid numbers, water contents, and viscosities. Meanwhile, stability and corrosion properties of bio-oil were also promoted [66]. Junming et al. [67] reported their observations on ozone oxidation of bio-oil, and production of upgraded bio-oil using subsequent esterification.

Yao et al. [68] and Zhou et al. [70] analyzed the component of esterified bio-oil using gas chromatography/mass spectroscopy (GC/MS) and Fourier transform infrared spectroscopy (FTIR). The former detected that 1,1-dimethoxypropan-2-one was the most abundant species in the fraction of 60–80 °C. Phenols were the most abundant species in the residue, followed by the ketones and hydrocarbons. The latter [70] demonstrated that upgrading significantly improved the dispersity of organic droplets in the bio-oil and completely removed char particles from the bio-oil. However, heavy species are still the main components in the upgraded bio-oil.

In recent years, there were many investigations [71–74] into upgrading bio-oil through catalytic esterification reaction using solid acid catalysts in China. The results consistently indicated that the solid acid catalyst had a high catalytic activity to convert organic acids, such as formic acid, propionic acid and acetic acid, into esters effectively. Meanwhile, properties of bio-oil, such as stability and fluidity, etc., could be improved.

3.9. Emulsification

In order to promote the application of bio-oil as a combustion fuel, emulsification was performed as a feasible method to upgrade the bio-oil. The research by Guoli et al. [75] demonstrated that emulsion was a cheaper and convenient method for utilization of bio-oil.

With the help of surfactants, pyrolysis oils can be emulsified with diesel. Zuogang et al. [76] produced bio-oil emulsion fuels using bio-oil and 0# diesel by power ultrasound. They studied the effects of treating time and ultrasound power on stability of the emulsion fuels. The results indicated that the emulsion fuels with a stable time as long as 35 h could be obtained under ultrasound power of 80 W with a treating time of 3 min.

Wang [77] investigated the combustion characteristics of a blend fuel of bio-oil and diesel with different proportion of the two fuels using a numerical simulation method. The factors, such as combustion components distribution, ignition delay and temperature distribution in the combustor were studied.

Xu et al. [78] studied the lubricity of the bio-oil/diesel fuel using a High Frequency Reciprocating Test Rig (HFRR). They found that the lubrication ability of the bio-oil/diesel fuel was better compared with the conventional diesel fuel (number zero). Qiang et al. [79] conducted bio-oil emulsification with different percentages of diesel oil, and evaluated the lubrication properties of oil samples using a four-ball tester. They found that several properties, such as friction-reduction, anti-wear and extreme-pressure were better, which were not consistent with the conclusion of Xu et al. [78]. The difference was likely to be caused by use of the different device in their experiments. Meanwhile, increasing content of the bio-oil in the emulsions could promote the lubrication ability of the emulsions. Moreover, the solid char particles in the pyrolysis bio-oil could enhance its lubrication performance.

Jiang et al. [80–83] reported their researches about upgrading the storage properties and thermal stability of bio-oil through emulsification with biodiesel. During the aging research, a slight decrease in acid numbers and a slight increase in the molecular weight were observed and ES/biodiesel blends are stable under the conditions used in the research.

To conclude, using emulsification with diesel oil is a relatively simple and effective way of upgrading bio-oil. It is a short-term method for the application of pyrolysis bio-oil in diesel engines and other devices. This method can improve some properties of bio-oil, such as ignition characteristics, but it is still difficult to promote other fuel properties, such as heating value, corrosivity, cetane number and so on, to a satisfied degree. Besides, emulsification required a large input of energy for high production of emulsions. At present, the majority of bio-oil dosage in the emulsification investigation is less than 400 ml. Moreover, design, testing and production of injectors and fuel pumps with higher efficiency are urgently needed.

3.10. Industrial application of bio-oil

Many substances, such as aromatics, olefins, resins, etc., can be extracted from the pyrolysis bio-oil for practical industrial application. Recently in China, Zhao et al. [84] extracted aromatics via catalytic pyrolysis of pyrolytic lignins from bio-oil. The results indicated that without catalysts the main products were phenols with a selectivity of above 90% at 600 °C, which demonstrated that it was an alternative way to produce useful chemicals and fuel additives. Gong et al. [85] performed the selective production of light olefins from catalytic cracking of bio-oil using the La/HZSM-5 catalyst. Light olefin is a kind of basic building blocks for the petrochemical industry. Similarly, many other chemical products could be produced using pyrolysis bio-oil as feedstock. In summary, it is crucial for Chinese researchers to develop more reliable low cost refining and separation techniques before industrial production of chemicals from bio-oils is fully realized.

4. Conclusions and recommendations for future work

4.1. Conclusions

Biomass pyrolysis is one of the most promising methods in production of bio-oil, which has great development potential around the world. Due to the advantages in economic problems and environmental protection, bio-oil as a new substitute of fossil fuels, has acquired extensive recognition globally. Researches demonstrated that pyrolysis bio-oil could be upgraded using various approaches, such as hydrogenation, hydrodeoxygenation, catalytic pyrolysis, catalytic cracking, steam reforming, molecular distillation, supercritical fluids, esterification and emulsification, etc. Conducting such research is very important to offer basic information for the application of bio-oil from biomass fast pyrolysis in the world. In addition, the commercialization of bio-oil upgrading technology needs to be developed further. In short, conclusions can be drawn as follows:

(1) the one-step hydrogenation–esterification (OHE) method is much better than the traditional method due to the use of bifunctional catalysts.
(2) Like amorphous catalysts, more novel and economical catalysts that can be used for hydrodeoxygenation of bio-oil with high oxygen content should be further developed.
(3) Catalytic pyrolysis can promote the production and quality of bio-oils by using the appropriate catalysts while it encounters some critical problems, such as catalyst deactivation, reactor clogging, coke production and high water content in bio-oils, etc.
(4) The integrated upgrading process of catalytic pyrolysis and catalytic cracking has the superiority of increasing the liquid yield and improving the fuel quality over the separate processes.
(5) It is feasible to upgrade bio-oil by steam reforming in China but needs appropriate catalysts.
(6) Upgrading bio-oil using molecular distillation is appropriate for the separation of bio-oil and is not restricted by its poor properties, but is energy-consuming generally.
(7) Using supercritical fluids (SCFs) is not economically feasible to upgrade bio-oil on a large scale due to the high cost of the organic solvents.

4.2. Recommendations for future work

The components of bio-oil are very complex. On one hand, the pyrolysis bio-oil has many advantages in properties, such as less toxic, good lubricity and stronger biodegradation and so on. On the other hand, it also has lots of disadvantages in characteristics, that is, high contents of water, oxygen, ash and solids, low pH value, high viscosity, chemical and thermal instability, low heating value, and poor ignition and combustion properties. Although the upgraded bio-oil could be used as alternative fuel of boiler and internal combustion engine, now it still cannot replace the fossil fuels completely due to the restriction in technologies and costing. How to develop and use the upgrading technologies to realize the industrial application of bio-oil from biomass pyrolysis is a big matter. In order to facilitate this issue, great efforts should be paid in the following aspects in the future:

(1) more appropriate catalysts (e.g., bifunctional catalysts or multifunctional catalysts) and dependable, steady and fully developed reactor systems need to be developed in the future.
(2) During the upgrading of bio-oil using various catalysts, the mechanism on catalyst deactivation needed to be further explained, and the catalysts with high durability, strong renewable ability and high efficiency need to be developed urgently.
(3) During the researches on emulsification, seeking for more economic and abundant surfactants as substitutes for the high-priced surfactants remains an interesting topic to investigate.
(4) The researches on how to combine pyrolysis reactors with reaction conditions organically and how to efficiently use upgrading technologies of other oils for reference need to be done in the future so that new ideas would be found.
(5) In order to promote the industrialization of upgrading of bio-oil, more efforts should be paid to develop more experimental facilities with larger scale and high efficiency.

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